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Hydrogen bonding effects in perfluorinated polyamides: An investigation based on infrared spectroscopy and density functional theory calculations

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ABSTRACT

The IR spectra of solutions of a perfluorinated polyamide in different solvents are analyzed in the spectral range of "free NH" stretching modes, in order to study the effects of hydrogen bonding in determining the unusual spectral behaviour observed for these systems. The presence of different bands in the spectral range associated to NH bonds with the H atom *not* involved in hydrogen bonding and their evolution with the polymer concentration has shown that free NH bonds have a different nature depending on the occurrence of hydrogen bonding on *neighbour* atoms and on the configuration of the molecular complexes in which they are involved. These differences have been interpreted on the basis of DFT (B3LYP/6-311++G**) computations on suitable molecular models that allowed a qualitative and quantitative rationalization of the chemical–physical effects involved. The computational analysis points out the subtle intramolecular and intermolecular vibrational effects occurring in these systems and brings to an interpretation and assignment of the IR spectra which goes over the interpretations usually adopted when dealing with the vibrational spectroscopy of hydrogen bonded polymers and molecules.

1. Introduction

Neutral non-functionalized perfluoropolyethers (PFPEs) are a family of macromolecules composed only by carbon, oxygen and fluorine. They have been known since more than 40 years [1] and are well established as high-end lubricants when harsh applicative conditions are to be addressed [2]. The presence of a fully fluorinated shell around the C–C backbone guarantees high thermal resistance, combined with oxidative and chemical stability; while ether bonds confer high flexibility to the polymeric chain. Consequently, they are liquid at very low temperature and characterized by a very smooth variation of viscosity with temperature [3]. For this reason they are successfully employed, for example, in the automotive industry where lubricants able to operate in temperature ranges spanning from −40 °C to 130 °C are mandatory [4]. Like all the fluorinated materials they possess low surface energy, a good wetting behavior with respect to both high and low energy surfaces, and a low density of cohesive energy. Moreover, they show large permeability to vapors and gases; for this reason, their anti-rust and antiwear properties, when applied to metals, result to be lower than other classes of synthetic lubricants [5]. The formulation with additives is a very common procedure to improve the performances of lubricants [6]. Unfortunately, conventional additives, specifically designed for conventional non fluorinated oils, are not soluble in PFPE oils and consequently the additivation of perfluorinated lubricants still represents a problem which is only partially solved. Indeed, matching the additive solubility (necessary for a stable formulation), with its efficiency is not an easy task: the first feature would imply molecules showing a low solubility parameter, while the second objective suggests to chose a molecule characterized by a relatively high solubility parameter.

Three different technological platforms have been exploited at industrial level for the preparation of PFPEs [7]. The photooxidation of perfluoroolefins is the most versatile, giving access, through a proper selection of the monomer and of the key parameters of the process, not only to different neutral compounds in a wide range of molecular weights, but also to PFPEs bearing a variety of functional groups (functional PFPEs). Recently, several functional PFPEs have been described in the literature as soluble additives for PFPEs lubricant oils [8]. Among them amides of formula (1) have proved to be particularly effective in improving their anti-rust performances.

$$CF_3O[CF_2CF(CF_3)O]_p[CF_2O]_qCF_2C(O)NH_2 \qquad (1)$$

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The mechanism behind the corrosion inhibition is still under debate, but it is generally recognized to happen through the formation of an adsorbed layer of the additive on the metal surface, through either physical or chemical interactions [9]. Organic nitrogen-containing molecules like (1), are adsorbed by means of the surface-active NH_2 group that forms a chemisorptive bond with the metal surface. The apolar tails orient away from the interface toward the bulk oil, providing further protection through the formation of a hydrophobic network that prevents water and aggressive ions to reach the metal surface [10]. Usually soluble organic inhibitors produce a protective layer that is only a few molecules thick, whereas insoluble inhibitors, dispersed in the fluid, can build films reaching thickness of several tens of nanometers [11]. One of the main mechanisms causing a rust-inhibited oil to fail to protect a metal surface is the depletion of the protective layer by the leaching action of the water contacting it. The additive should therefore be available in a concentration able to assure a rate of adsorption fast enough to repair this kind of damages. The mechanism and the ability of the molecule to adsorb on a substrate is a balance of difference forces: solute–solvent interactions, solute-substrate affinity, intermolecular aggregations and diffusivity of single or aggregated molecules. Hydrogen bonding, when structurally possible, is one of the most efficient process ruling the intermolecular associations, as for example in the case of amide (1). These bonds among two or more molecules can be described in terms of fraction of aggregates and average number of molecules per aggregate, depend also on the concentration and can affect deeply the macroscopic behaviour of the compound.

Therefore, the understanding of the solubility of the additive in the base oil and of its aggregation behavior is a useful tool to finally select and optimize the dosage needed to assure protection in correlation with specific tests.

In the present study the hydrogen-bonding behavior of the amide (1) has been studied through FTIR spectroscopy and density functional theory (DFT) calculations in order to understand the molecular phenomena ruling the macroscopic properties of these systems. It is indeed well-know [12] that vibrational spectroscopy is a powerful technique for the investigation of hydrogen-bonding effects due to the existence of peculiar markers in the IR (and Raman) spectra. However, both the interpretation of the spectra and the possibility to extract quantitative information from IR intensities rely on a well-established assignment of the observed bands. This assignment is particular tricky in the case of the amide (1) due to a peculiar behaviour which goes beyond the commonly observed features of hydrogen bonded species. The analysis of IR spectra and a suitable modeling reveal indeed that both intermolecular and vibrational effects cannot be interpreted straightforwardly and require a deep investigation of the different interactions taking place at the molecular level.

2. Experimental and computational details

2.1. Synthesis

The additive (1), $CF_3O[CF_2CF(CF_3)O]_p[CF_2O]_qCF_2C(O)NH_2$ ($q << p$), has been prepared by condensation of ammonia with the PFPE ester of formula (2):

$$CF_3O[CF_2CF(CF_3)O]_p[CF_2O]_qCF_2C(O)CH_3 \quad q << p \tag{2}$$

However, this ester is derived from the corresponding acid that contains significant quantities of ketone-terminated and neutral species, (3) and (4) structures, respectively.

$$CF_3O[CF_2CF(CF_3)O]_p[CF_2O]_qCF_2C(O)CF_3 \tag{3}$$

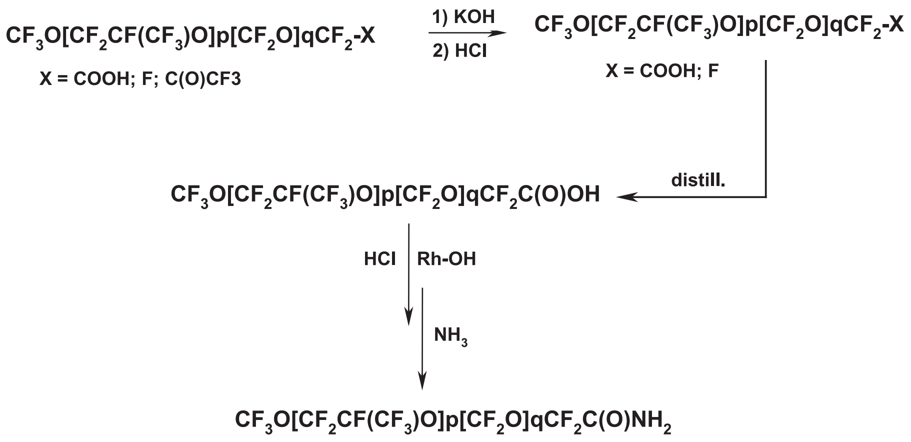
$$CF_3O[CF_2CF(CF_3)O]_p[CF_2O]_qCF_3 \tag{4}$$

Ketones can be eliminated by treating the acid with strong base at 80 °C; each terminal ketone can generate a PFPE–COOH or a PFPE–CF_3, depending on the C–C bond which is broken.

Subsequently, the acid that contains as mixture neutral species is further purified by eliminating the more volatile neutral species by distillation at alkaline pH.

Finally, the acid is esterified by acidic condensation with a primary alcohol (i.e. *iso*-buthanol).

The following scheme summarizes the reactions described above:



The result of the synthesis here described will be called hereinafter “*Amide*”.

2.2. Experimental Setup

IR and Raman spectra have been recorded with a Thermo Nicolet Nexus® 870 FTIR instrument equipped with a FT-Raman module; the sample was kept in a suitable liquid cell with fixed optical pathlenght equal to 1 mm. The acquisition parameters of IR spectra were 256 scans for each spectrum and a spectral resolution

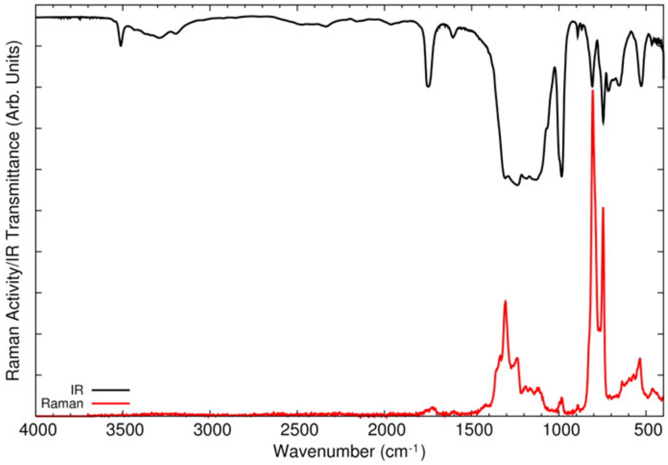


Fig. 1. Experimental IR and Raman spectra of pure Amide.

of 2 cm^{-1}. The FT-Raman spectra have been recorded with a nominal laser power at sample around 200 mW (NdYag laser, 1064 nm), 1024 scans and a spectral resolution of 2 cm^{-1}. IR and Raman spectra of Amide are reported in Fig. 1.

2.3. DFT calculations

DFT calculations on suitable molecular models have been carried out for a detailed investigation of the effects of hydrogen bonding on the infrared spectra of Amide (see Fig. 3). We used the Gaussian 03 package [13] and we chose B3LYP exchange-correlation functional [14] and 6-311++G** basis set.

As already verified in previous works [15,16], the effect of basis set superposition error (BSSE) on vibrational frequencies is negligible, even if poor basis sets are used [17], for this reason we did not apply any kind of correction for BSSE during geometry optimization and frequency calculations; however we apply counterpoise correction (CP) [18] on the final geometries for a correct evaluation of the interaction energies (see Table 1).

The geometry of the complexes has been fully optimized without any kind of constraint: some different trial structures representative of the different kind of hydrogen-bonded complexes have been considered and the resulting diverse optimized complexes are shown in Fig. 3.[1] All the frequency values (except those generated by fitting, see Section 3.4) have been scaled by 0.9688, as indicated in the work by Merrick et al. [19].

3. Results and discussion

3.1. Experimental IR spectra

In Fig. 2 the experimental IR spectra of Amide dissolved in three different solvents at increasing concentrations (weight/weight) are reported.

In particular, the three selected solvents are: FOMBLIN®M03, GALDEN®D02, H-GALDEN®ZV60.

Their formulas are the following:

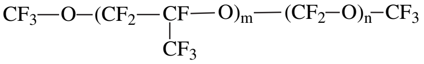
-FOMBLIN®M03 PFPE, fully fluorinated linear PFPE:

$$CF_3{-}O{-}(CF_2{-}CF_2{-}O)_p{-}(CF_2{-}O)_q{-}CF_3$$

$$(M_n \approx 4000,\ 1.5 < p/q < \ 2)$$

-GALDEN®D02 Y25 PFPE: fully fluorinated branched PFPE:

$$(M_n \approx 750, m >> 1)$$



$$CF_3{-}O{-}(CF_2{-}\underset{\displaystyle CF_3}{\underset{|}{CF}}{-}O)_m{-}(CF_2{-}O)_n{-}CF_3$$

-H-GALDEN®ZV60 PFPE: fluorinated linear PFPE, end-capped by a difluoromethylic groups:

$$CF_2H{-}O{-}(CF_2{-}CF_2{-}O)_p{-}(CF_2{-}O)_q{-}CF_2H$$

$$(M_n \approx 230,\ 1.5 < p/q < \ 2)$$

These solvents represent almost all possible PFPE structures: fully fluorinated linear and branched chains, and (per)fluorinated chains with polar end groups.

When the first two solvents are considered a peculiar spectral evolution with concentration is observed between 3570 and 3400 cm^{-1}, i. e. in the spectral range usually assigned to NH stretchings of bonds not involved in hydrogen bridges (called "free" NH bonds in the following). At lower frequency the broad band commonly assigned [12,20] to H-bonded NH stretching is observed (3375 cm^{-1}); as expected, while increasing the polymer concentration this band steadily grows up.

However, at the same time several other components gain more and more intensity in the "free NH" stretching region, while the two bands assigned to symmetric and antisymmetric NH stretching of the NH bonds of the "isolated" (no hydrogen bond) molecule (at about 3560 and 3440 cm^{-1}) lose their intensity, consistently with the increased amount of hydrogen bonded complexes.

The presence of different "types" of free NH bond cannot be interpreted straightforwardly and needs a careful analysis.

Based on the fact that stretching vibrations involving H atoms are extremely sensitive to the intramolecular structure of the molecule and to the surrounding environment, as shown by Mckean in the case of CH stretching modes [21], the appearance of several components in the NH stretching region can be interpreted as the evidence of the presence of different types of "free" NH bonds in our samples.

In each molecule, three sites are available for hydrogen bonding, i.e. the C=O bonds and each of the two NH bonds but actually hydrogen bonding is responsible for a reorganization of the electronic structure which is not confined to the two atoms which form the bridge: changes may affect also the nearby atoms in the molecule, in particular the "free" NH bond adjacent to a C=O or to a NH bond engaged in the H bridge.

It is hardly expected, in our case, that both of the NH bonds belonging to the same NH_2 group are simultaneously donors in two H bridges, since this would introduce sterical hindrance and would require a well-defined supramolecular geometrical arrangement, which is not expected for polymers in solution; moreover when a H bridge is formed by a H donor the "acidity character" of the second H of the same molecule is reduced and this lowers its ability to act

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[1] Conformational effects on the IR spectra in the NH stretchings region have been investigated by carrying out preliminary calculations on few different conformers (isolated molecule) and no significant effects have been found. The trial starting geometries for dimers and trimers have been generated by employing two/three monomers with the final optimized geometry of the isolated molecule (Fig. 3a) and with different relative orientations. In these cases, the starting conformation of the molecules is that of the optimized isolated molecule (minimum energy conformer) but all the geometrical parameters (both the intramolecular and intermolecular ones) of the model complexes have been completely optimized. In the Supplementary Material these geometrical parameters are reported for each model considered.

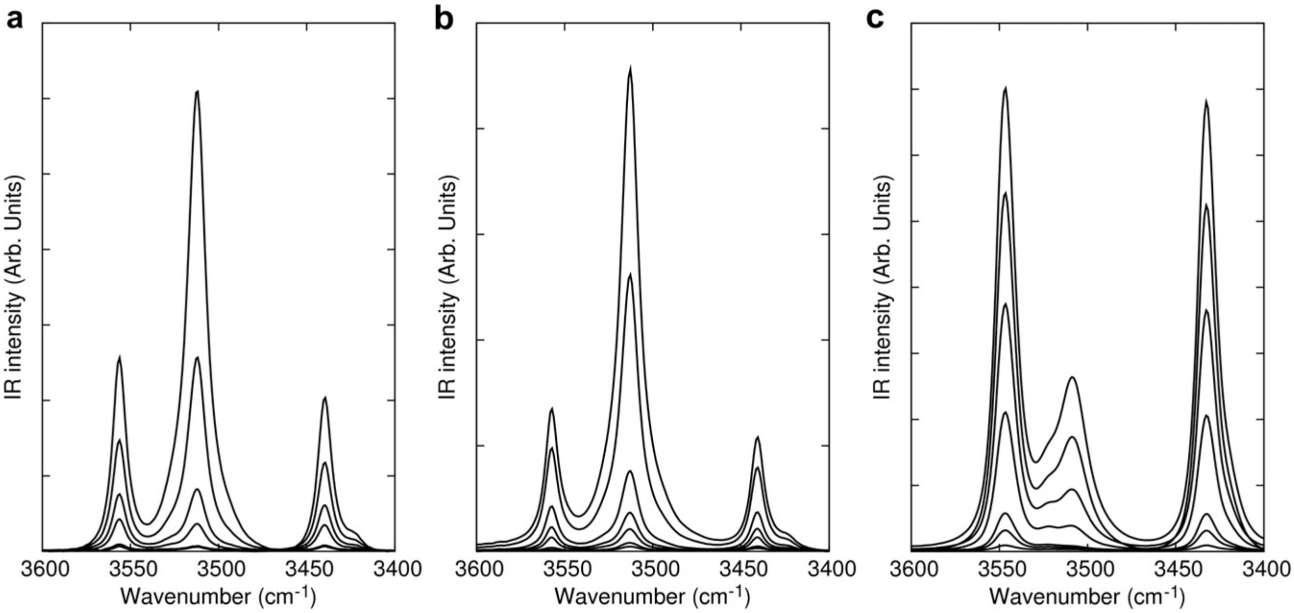

Fig. 2. Experimental IR spectra of different solutions for increasing concentration of the Amide molecules a) FOMBLIN®M03 solution in concentrations from 0.019% to 1.11% b) GALDEN®D02 solution in concentrations from 0.019% to 1.85% c) H-GALDEN®ZV60 solution in concentrations from 0.037% to 7.41%. Spectral subtractions with pure matrix are reported.

as H-bonding donor. This qualitative description is indeed in agreement with atomic charges derived from DFT computed atomic polar tensors [22], as shown in Fig S1 of the Supplementary Material.

For this reason we can make the hypothesis that, depending on the geometrical structures of hydrogen-bonded complexes, different types of structures can occur where at least one of the NH bond is still "free", thus giving rise to several bands in the free NH stretching frequency range.

As already discussed, these bands would not fall at the same frequencies seen in the fully isolated molecule: depending of the kind of complex (H bond involving one of the two NH, or the C=O group, or both NH and C=O) the non-bonded NH stretching in the complex would feel a different environment that modifies slightly the electronic structure. This generates a different stretching force constant value and thus a different frequency.

Accordingly, it could be supposed that the specific frequency of each band in the free NH stretching region could be considered a marker of a given type of bond. We will show that this is only partially true; indeed the frequency behaviour is further complicated by the dynamical vibrational coupling, mainly involving the adjacent NH bond in the molecule: this coupling still occurs even if one of the NH bonds is involved in hydrogen bonding. The sensitivity of the NH stretching frequency and the tendency of the related normal mode not to be perfectly localized was already underlined also in a previous work by Mirkin et al. [23]. Furthermore, Skrovanek et al. [20] discussed the frequency and intensity evolution of the free NH stretchings bands for increasing temperature in amorphous polyamides and Nylon-11 samples: they demonstrate that this evolution cannot be directly related to the strength and abundance of hydrogen bonds.

In the last solvent considered in this work (H-GALDEN® ZV60), a completely different behaviour is observed, as illustrated in Fig. 2: here, by increasing the concentration of the polymer the peculiar evolution of the free NH stretchings bands is not observed.

The analysis of these results requires a theoretical investigation based on suitable modeling with the aim to clarify the experimental observation and to describe in details the chemical-physical phenomena involved.

3.2. DFT calculations of IR spectra of molecular models

In order to investigate the effect of different kinds of hydrogen bonding on the IR spectra in the NH frequency range the existence of different structures should be taken into account, namely:

i Molecules where no H-bonds are present (isolated molecule, Fig. 3a)
ii Dimers where the donor molecule form *one only hydrogen* bond (through NH) with the acceptor one (through C=O): this complex presents three unequivalent free NH (see, for instance, Fig. 3b and d)
iii Dimers where *two H-bonds* are present at the same time: in this case each molecule is simultaneously donor (through a NH bond) and acceptor (through C=O) and the complex shows two (equivalent) free NH bond (see Fig. 3c)
iv Trimers where each molecule is simultaneously donor and acceptor, in a similar way as case (ii) (Fig. 3g and f)
v Moreover the occurrence of dimers without any H bond can be considered, hold together by dipole–dipole interaction (Fig. 3e) or electrostatic H…F interactions.

It has to be noticed that these molecular models are chemically different from the experimental samples, due to the absence of the oxygen of the ether group in their chemical structure. This choice is motivated by two facts:

a) Our study aims at an interpretation of hydrogen bonding effects in perfluorinated amides on a general ground. For this reason, we chose a representative model which could be completely general and transferable to the interpretation of similar molecules.
b) Due to the absence of relevant intramolecular vibrational interactions we do not expect a significant difference on the NH stretching frequencies and intensities caused by the presence of the ether oxygen along the molecular chain. In order to prove the above statement, we carried out a calculation on suitable model system (CF_3–O–CF_2–($CFCF_3$)–O–CF_2–($CONH_2$)): the differences in NH stretching frequencies and intensities are

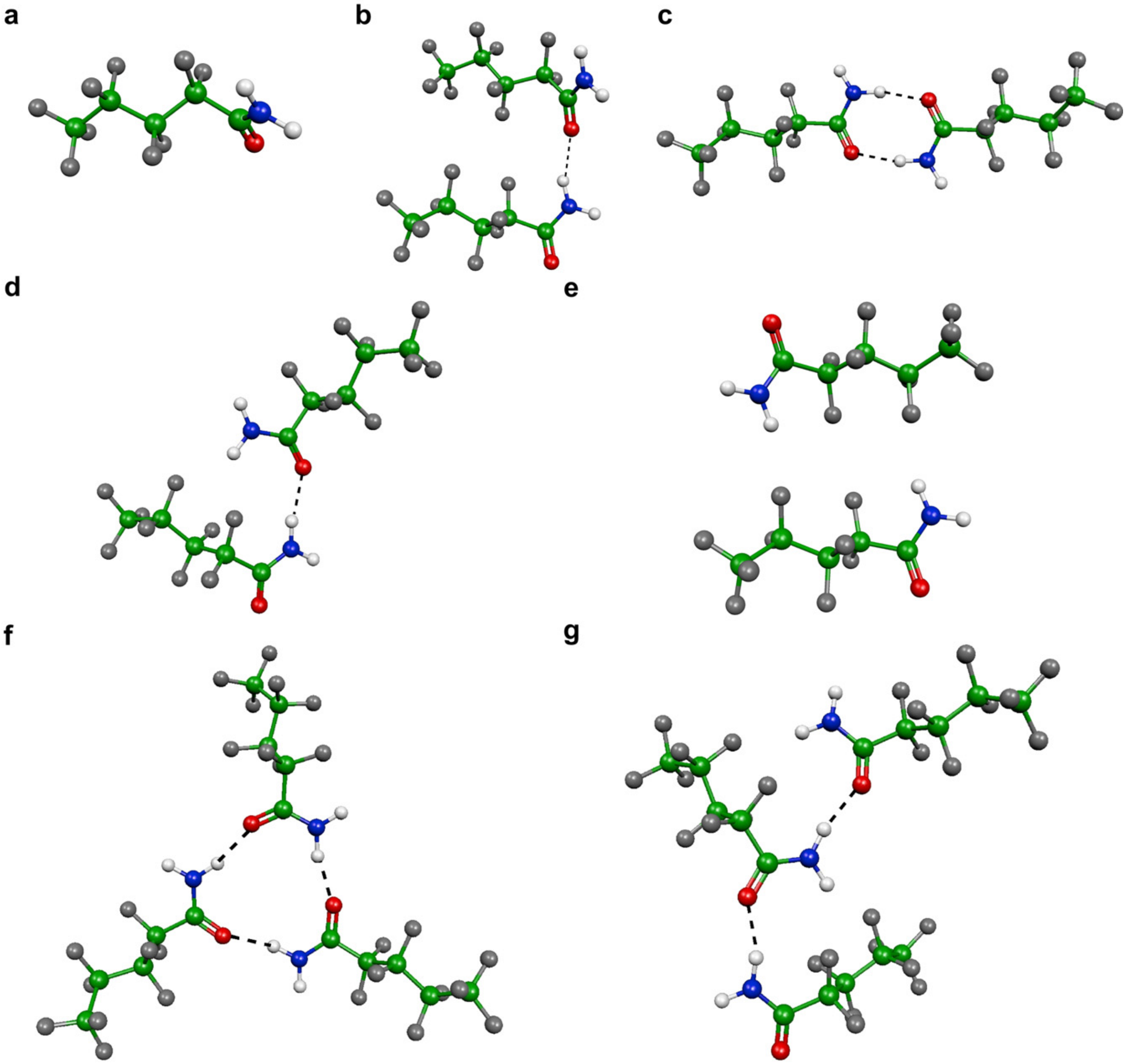

Fig. 3. Sketches of the models (isolated molecule, dimers and trimers) investigated by means of B3LYP/6-311++G** calculations: a) isolated molecule, b) dimer 1, c) dimer 2, d) dimer 3 e) dimer 4, f) trimer 1, g) trimer 2.

completely negligible ($\Delta\nu < 1$ cm^{-1}, $\Delta I < 1$ km/mol) and confirms the validity of our approach. Moreover, the transferability of the models shown in Fig. 3 for the discussion of the spectral features in the NH stretching frequency range is demonstrated.

Table 1
Intermolecular interaction energy of the dimers sketched in Fig. 3. These energies have been computed on the basis of B3LYP/6-311++G** corrected for BSSE with the counterpoise correction [18]. The interaction energy is defined as $E^{\text{int}} = E^{\text{dimer}} - 2 \times E^{\text{isolated}}$ where E^{dimer} is the energy of the dimer and E^{isolated} the energy of the isolated molecule.

Model	Interaction energy (kcal/mol)
Dimer 1	−4.10
Dimer 2	−12.50
Dimer 3	−6.60
Dimer 4	−1.42

The structures reported in Fig. 3 are the final results of the optimization of several possible starting geometries. For each of these optimized geometries the computation of IR spectra was carried out, as reported in Fig. 4. From this figure it can be clearly seen that, according to the different structure considered, several bands at different frequencies (Table 2) are predicted in the region of the free NH bonds stretching (from 3650 to 3400 cm^{-1}). This finding confirms the ideas suggested in Section 3.1 about the different features of the free NH bonds depending on the environment that they feel both at the intramolecular and intermolecular levels. Accordingly, the IR spectra offer distinct frequency markers, which, in principle, may allow to identify the specific hydrogen bonded complexes occurring in a sample by inspection of the bands associated to free NH bonds.

However, a further vibrational effect plays a significant role and must be taken into account: in the case of the free NH bonds belonging to a donor molecule, one could expect that a H bond on

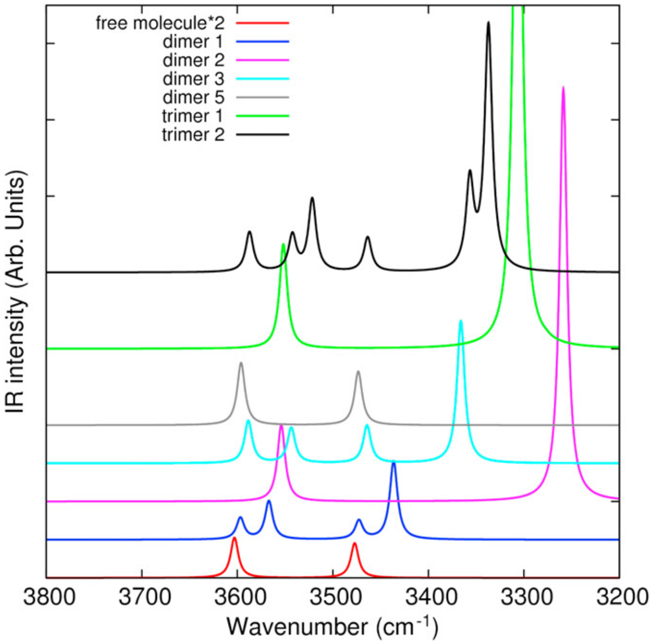

Fig. 4. DFT computed IR spectra in the NH stretching frequency range for the models sketched in Fig. 3 (frequencies scaled by the factor 0.9688).

the adjacent NH could decouple dynamically its NH stretchings, giving rise to the bands of two independent local NH oscillators, whereas the isolated molecule shows two normal modes involving vibrations of the whole NH_2 group (r^+ and r^-, namely symmetric and antysimmetric stretchings). A deeper vibrational analysis, based on the discussion of the computed vibrational eigenvectors demonstrates that this is not the case, since the dynamical coupling is still important.

Table 2
Computed values (B3LYP/6-311++G**) of frequencies (cm^{-1}) and IR intensities (km/mol) for the models shown in Fig. 3 in the NH stretching frequency range. Frequency values have been scaled by 0.9688, according to Ref. [19].

	Frequency (cm^{-1})	IR intensity (km/mol)
Isolated	3477	71
	3603	83
Dimer 1	3436	322
	3472	76
	3567	158
	3597	88
Dimer 2	3217	0
	3258	1699
	3554	314
	3554	1
Dimer 3	3366	586
	3463	155
	3543	145
	3588	174
Dimer 4	3472	4
	3473	217
	3596	245
	3596	12
Trimer 1	3276	5
	3305	1480
	3307	1465
	3552	208
	3552	213
	3553	9
Trimer 2	3338	1006
	3357	361
	3463	142
	3522	297
	3542	145
	3587	164

On the other hand, for practical purposes, this fact does not bring to any restriction in the use of frequency markers for the identification of the different complexes; moreover the markers can be used for quantitative determinations based on the experimentally observed spectra. To this aim a fitting procedure of the experimental spectra (in the region of the free NH) with a theoretical spectrum built as a weighted sum of the predicted spectra of the relevant complexes is proposed and discussed in Section 3.4.

3.3. Analysis of isolated NH stretchings

In the previous section, the computed IR spectra of different complexes are reported. Each different structure suggests that the free NH bonds involved are different in their nature, because of the rearrangement of the electronic distribution in the molecule due to H bonding. In other words, the free NH bond of a molecule acting as donor in a dimer is expected to be different from a free NH bond of an acceptor molecule (through C═O group) and also from the NH bond of an isolated molecule or from the free NH of a molecule which is simultaneously donor and acceptor.

On the other hand, the dynamical couplings that take place also in presence of non-equivalent NH bonds interferes with the identification of any individual NH bonds directly from a band frequency and/or intensity. This behaviour is shown by the eigenvectors associated to NH stretching modes of the dimers in comparison with those of the isolated molecule, reported in Fig. S2 of the Supplementary Material. We can observe that the two NH stretching are still dynamically coupled even if one of the bond is involved in H-bonding. As a consequence the frequency of the bands assigned to the free NH stretching is determined by the intrinsic "nature" of the free NH bond but is perturbed by its dynamical coupling with the stretching of the adjacent (H bonded) NH bond. In other words, also the dynamical coupling implies shifts of the frequencies characteristic of "isolated" bonds.

A tool to better investigate theoretically these effects is suggested by the technique proposed and experimented by Mckean [21] for the characterization of unequivalent CH bonds, through the determination of the stretching frequency of "isolated" CH oscillators. In his work, he studied IR spectra of molecules where all but one CH bond were deuterated: in this way the single CH^1 oscillator is almost perfectly decoupled from the other CD oscillators, giving rise to a band at the frequency of the "isolated" CH stretching. Frequency values so obtained have been shown [21] to correlate very well with characteristic bond parameters like bond length, stretching force constant and bond dissociation energy.

In Fig. 5 we show the results obtained by calculations where we artificially substitute with deuterium all H atoms belonging to NH_2 groups except one: the case of the free molecule and that of the dimer 1 (Fig. 3b) are considered. Looking at these results, we can see that also in the case of the isolated molecule the two NH bonds are different according to their closeness to the C═O bond; for this reason the bands associated to isolated NH stretchings (in the deuterated models) show different frequency values.

In the case of the dimer 1 (Fig. 3b) two effects are observed:

(i) We obtain three different frequencies for the "isolated" NH stretching bands of the free NH, showing a non-negligible difference among them.
(ii) The band associated to the NH bond forming the hydrogen bridge is largely affected and shows the usual red shift and intensification expected upon formation of an H bond [12].

Furthermore, the two doublets found for the complex without any deuteration can be described as due to coupled vibrations of the two NH stretching belonging to the acceptor molecule and to

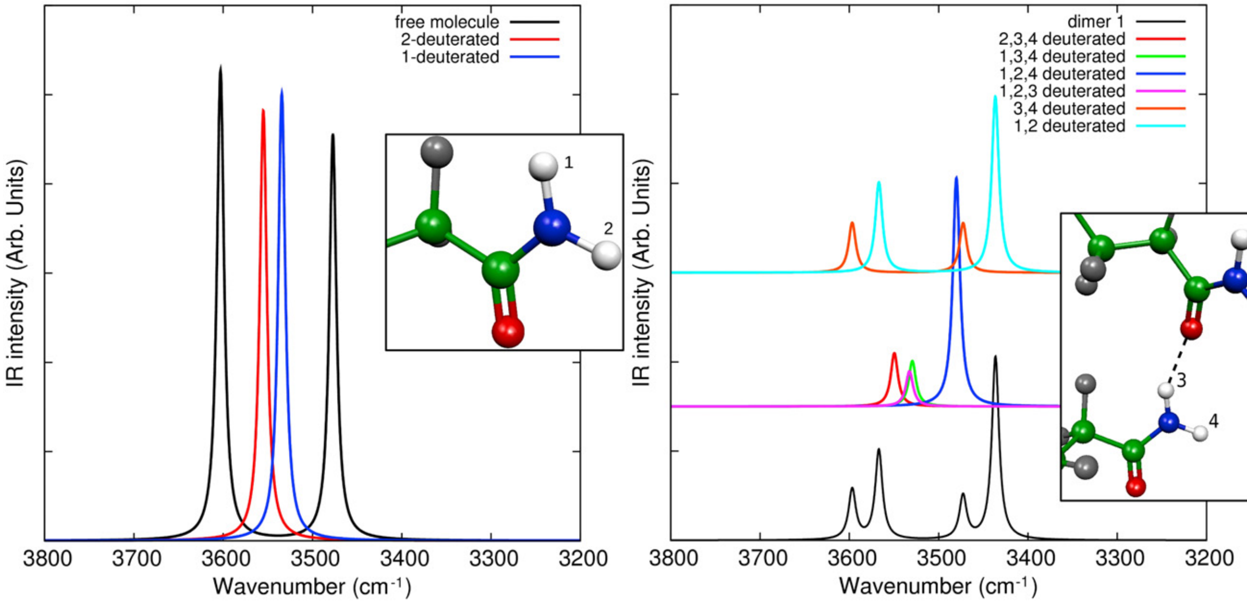

Fig. 5. Computed IR spectra for the isolated molecule (left) and dimer 1 (right) in the NH stretching frequency range; NH stretchings are isolated by selective deuteration (see text for further details). The labels of the H atoms involved are explicitly reported in the sketches.

the donor one respectively. This is directly proven by looking at Fig. 5 where the spectra obtained by deuterating pairs of H on the same molecule are shown, thus confirming what was already evident by inspection of the eigenvectors of Fig. S2. This confirms that the H-bonded NH bond, while being implicitly electronically and dynamically different, still remains dynamically coupled to the near free NH bond.

For sake of brevity, only the spectra of dimer 1 (Fig. 3b) is reported in Fig. 5; the phenomena occurring in the other complexes are similar, thus indicating that the observed frequencies result as a delicate balance between the occurrence of H-bonding and of dynamical couplings.

This can be analyzed in details looking at the data reported in Table 3 for the most interesting models.

The following discussion is based on the fact that isolated stretching frequencies and intensities are observables strictly correlated to the local characteristic of the bonds: we can then make some observation looking to the parameters relative to NH involved in the H bridge and free NH in different environment.

First of all, we can immediately realize that there are hydrogen bonds of different strength, according to the different complex structure.

As expected, the stronger H bridge corresponds to the case of dimer 2, where the presence of two H-bonds results in a more than additive stabilization effect: in this case we find the lowest NH stretching frequency (3257 cm^{-1}) for the H bonded NH and the highest intensity of the corresponding bands, which increases of one order of magnitude with respect to the case of the free NH of the isolated molecule.

The weaker H bond is that of dimer 1, showing a frequency of the H bonded NH of 3480 cm^{-1} and the lowest intensity found for a donor NH, which is however about 5 times the value characteristic of the free NH in the isolated molecule.

Interestingly, dimer 3 shows an intermediate value of isolated frequency and intensity for the donor NH bonds, thus suggesting that some interaction between a free NH of the acceptor molecule and fluorine atoms of the donor molecule contributes somehow to the complex (and to the H bond) stabilization. Indeed, the distance between the H atom in the NH bond and the F atom is 2.412 A which is smaller than the sum of Van der Waals radii of the two atoms (2.67 A); this fact indicates a strong electrostatic interaction between the two atoms which can be even considered as a hydrogen bond if the "Van der Waals cutoff" definition [12,24] is assumed.

Table 3

Values of frequencies (scaled by 0.9688) and intensities for isolated NH stretching of the models sketched in Fig. 3. These values are obtained from the results of DFT (B3LYP/6-311++G**) computations by using selective deuterations in order to dinamically isolate the different NH bonds (see text for details). Values for NH bonds where the H atom is involved in hydrogen bonding are reported in bold character. Bond 1 refers to the NH bond where the hydrogen is in trans-position with respect to the oxygen atoms of the C=O.

	NH str. frequency (cm^{-1}) – bond 1	IR intensity (km/mol) – bond 1	NH str. frequency (cm^{-1}) – bond 2	IR intensity (km/mol) – bond 2
Isolated	3556	76	3534	79
Dimer 1	3550	94	3529	80
	3480	**402**	3532	62
Dimer 2	3546	91	**3257**	**957**
	3546	91	**3257**	**957**
Dimer 3	3548	94	3513	220
	3394	**679**	3524	69
Trimer 2	3547	101	3514	195
	3365	**827**	3507	182
	3380	**752**	3525	67

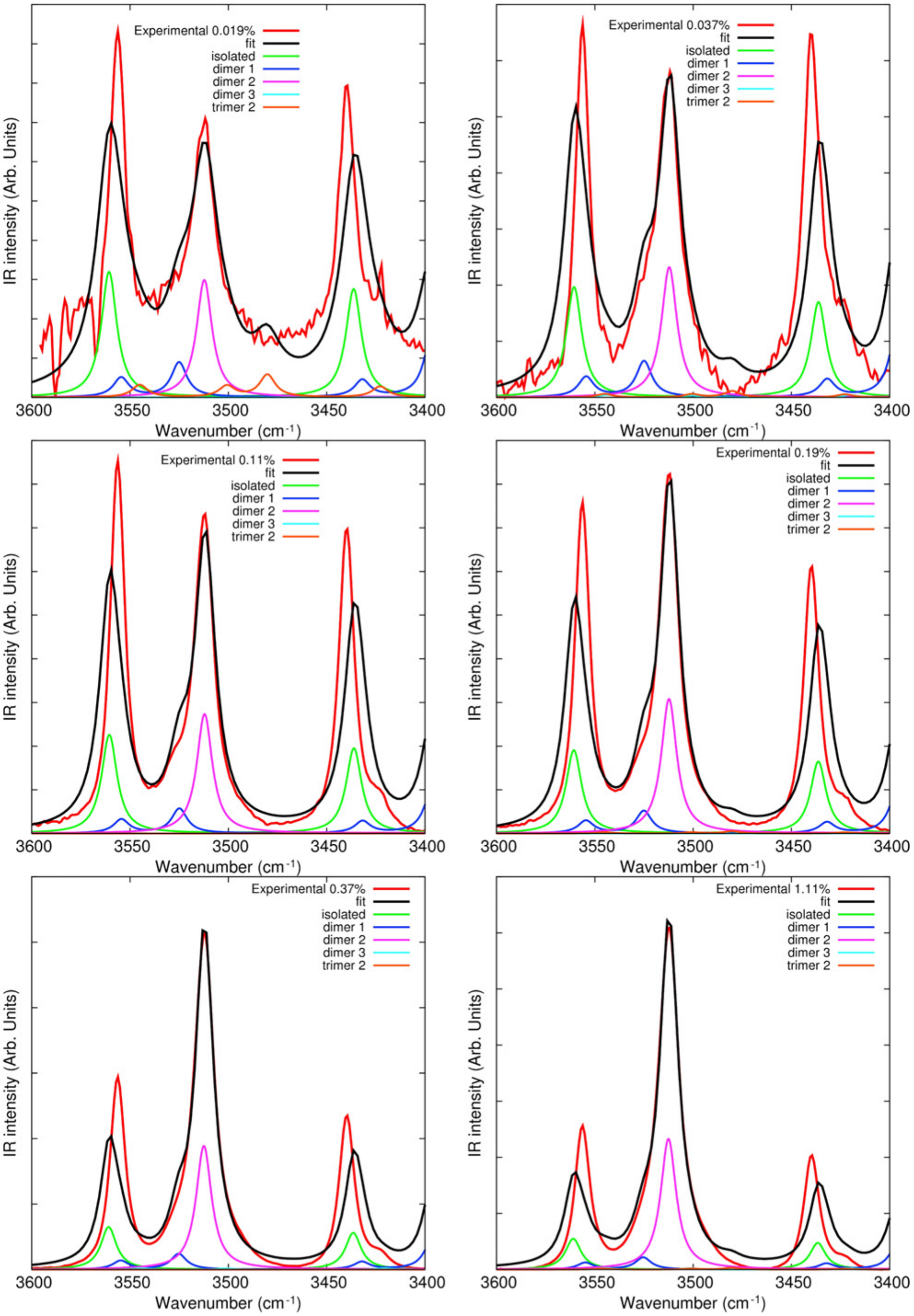

Fig. 6. Fitting of the experimental spectra of FOMBLIN®M03 solutions of increasing concentration of Amide with a theoretical spectrum built as a weighted sum of the computed spectra of the isolated molecule, dimer 1, dimer 2, dimer 3 and trimer 2. The coefficients of each contribution are determined by the fitting procedure (see text). The spectra of the individual models, multiplied for the resulting fitting coefficient, are also reported to clearly show their contribution to the fitting function.

A quite complicated situation is found for the trimer 2: the hydrogen bond involving the NH of the "middle" molecule (which acts simultaneously as donor and acceptor) approaches (both in frequency and intensity) the values found for the dimer 2 while the third (donor) molecule shows a NH bond similar to that of dimer 3.

As for the free NH bonds we find a variety of behaviours: already in the case of the isolated molecules the two inequivalent NH bonds differ in frequency by about 20 cm^{-1}, while their intensity is practically independent from the bond configuration with respect the C═O bond.

We find relatively small changes for the free NH of dimer 1, although in the case of the acceptor molecule some non-negligible frequency softening can be observed, for both NH bonds.

The larger frequency changes are found for the free NH of the acceptor molecule in dimer 3 showing a shift from 3534 cm^{-1} (isolated molecule, NH bond cis to C═O) to 3513 cm^{-1}. In this case there is also a remarkable increase of the stretching intensity of this "isolated" NH stretching band, which changes from 79 km/mol to 220 km/mol, suggesting an attractive electrostatic interaction between H and F non-bonded atoms. In a very similar way the intensity of two free NH of trimer 2 (those which are near to

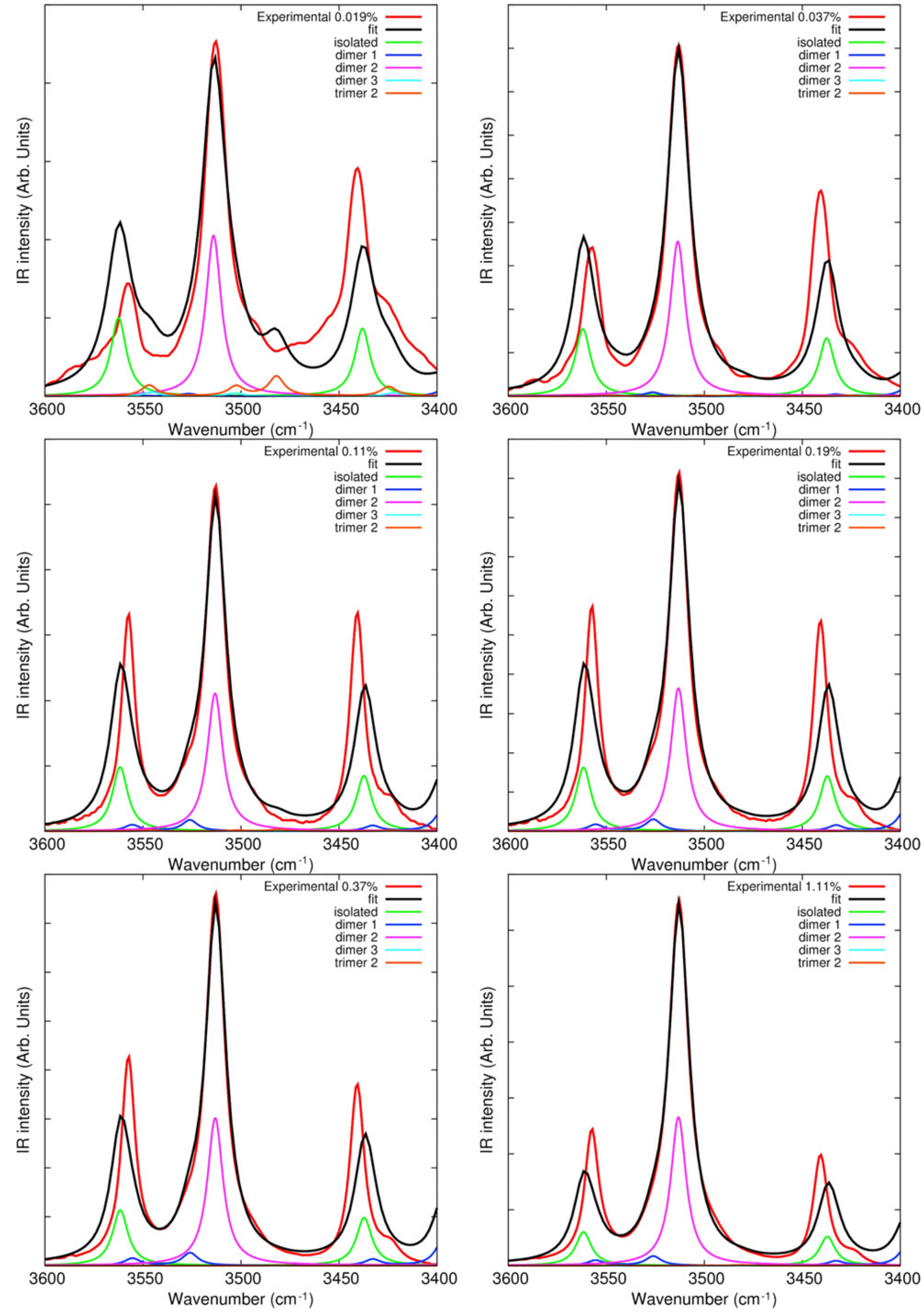

Fig. 7. Fitting of the experimental spectra of GALDEN®D02 solutions of increasing concentration of Amide with a theoretical spectrum built as a weighted sum of the computed spectra of the isolated molecule, dimer 1, dimer 2, dimer 3 and trimer 2. The coefficients of each contribution are determined by the fitting procedure (see text). The spectra of the individual models, multiplied for the resulting fitting coefficient, are also reported to clearly show their contribution to the fitting function.

fluorine atoms) increases to about 200 km/mol, with a remarkable frequency softening.

3.4. *Fitting of the experimental spectra*

In order to qualitatively and quantitatively investigate the evolution observed for the experimental IR spectra for increasing concentrations of the polymer, in terms of relative amount of the different complexes identified by DFT calculations, the spectra of Fig. 2 have been fitted with the computed ones. The fitting concerned only the free NH bond stretching region, ranging from 3600 cm^{-1} to 3400 cm^{-1} because the large broadening of the stretching bands associated to H bonded NH makes their fitting unreliable and it would not add any further information to our analysis of “free” NH bonds frequency range.

The function used for the fitting is built as a sum of the different computed bands (Lorentzian shape): the coefficients of the terms in the sum are determined by the best fitting of the experimental data at each concentration. Two further parameters determined by the fitting are the band width and the frequency scaling factors. The computed sum spectrum contains bands of selected complexes, which are chosen among the set of structures illustrated in Fig. 3 in

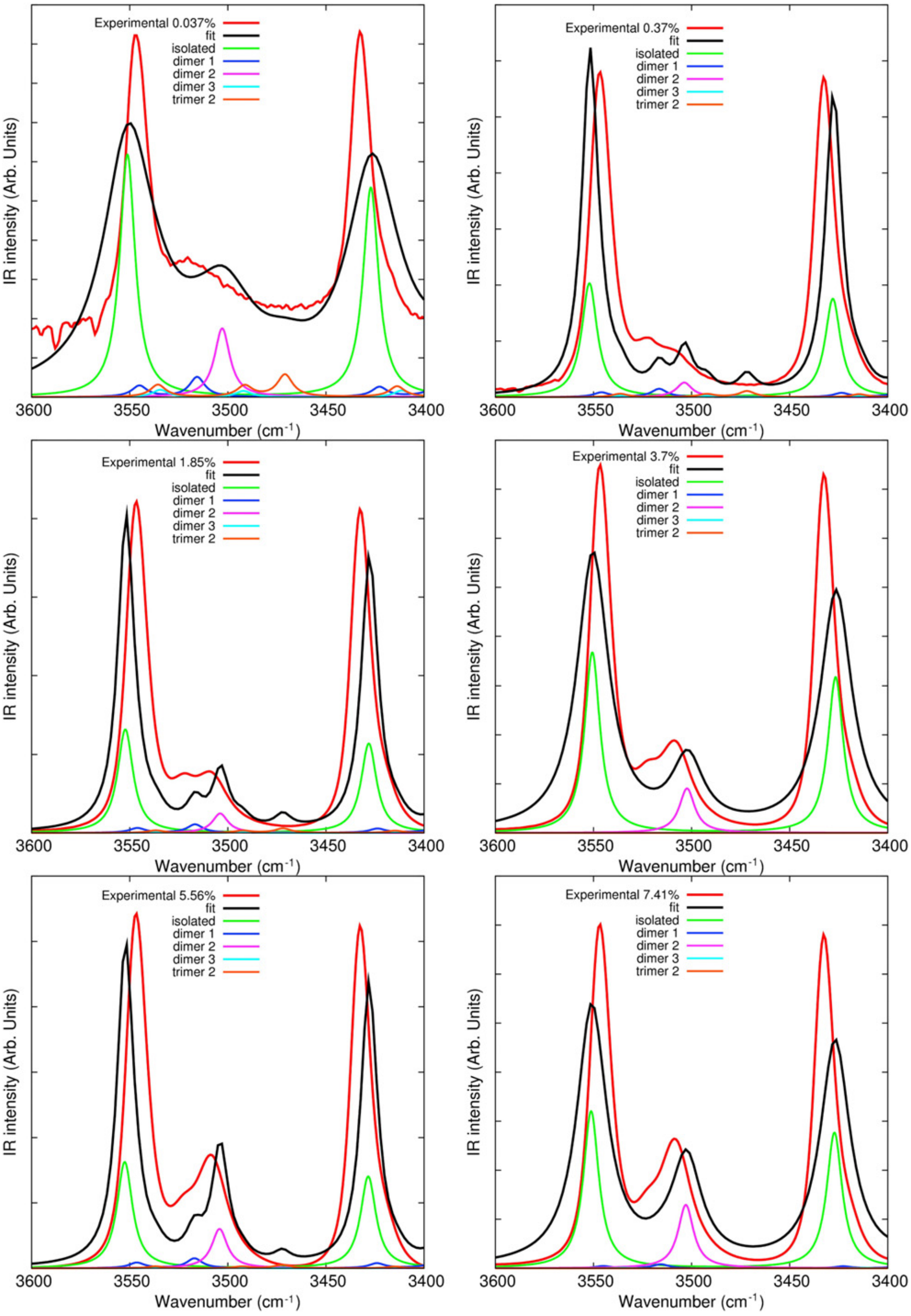

Fig. 8. Fitting of the experimental spectra of H-GALDEN®ZV60 solutions of increasing concentration of Amide with a theoretical spectrum built as a weighted sum of the computed spectra of the isolated molecule, dimer 1, dimer 2, dimer 3 and trimer 2. The coefficients of each contribution are determined by the fitting procedure (see text). The spectra of the individual models, multiplied for the resulting fitting coefficient, are also reported to clearly show their contribution to the fitting function.

order to consider only complexes showing well distinct spectral features.

To clarify this point, we can see in Fig. 4 that the band in the free NH bond stretching region of the dimer 2 (Fig. 3c) (3554 cm^{-1}) shows a frequency which matches that of the trimer 1 (Fig. 3f) (3552 cm^{-1}). In other words, this band does not allow to make a distinction of the two kind of complexes, but simply identifies a situation where the complex is characterized by two (or three) equivalent free NH bonds belonging to molecules which act simultaneously as donor and as acceptor of H bonds. For this reason, we introduce only the contribution of dimer 2 (Fig. 3c) in the fitting function: its weight in the sum spectrum giving the best fitting will be interpreted considering that it is representative of both the dimer 2 and the trimer 1.[2] Moreover, the dipole–dipole interacting molecules (Fig. 3e) are neglected in the fitting since

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[2] Actually the contribution of this trimer could be expected to be very small: as we can see the formation of a cyclic trimer requires a cooperative ordered geometrical arrangement of the three molecules involved. In our sample, the molecules are polymers in solution and thus the occurrence of such an arrangement could be deemed unlikely.

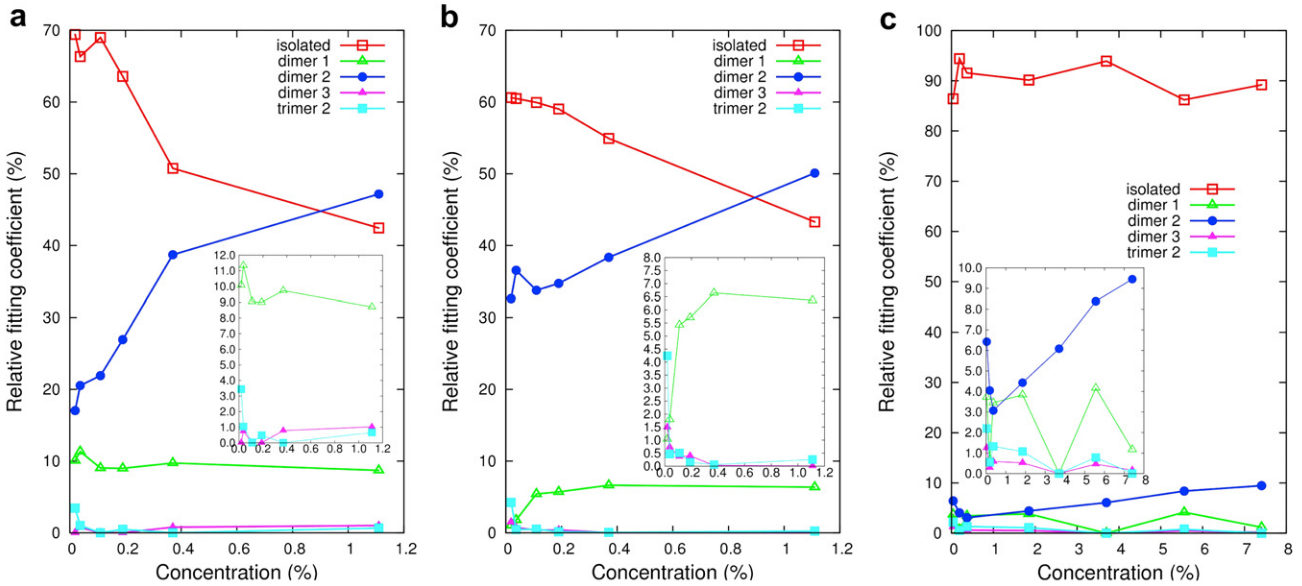

Fig. 9. Plots of the relative fitting coefficients (in %) as a function of concentration of Amide for the contributions used to build the fitting functions of Figs. 6–8. a) FOMBLIN®M03 solutions, b) GALDEN®D02 solutions, c) H-GALDEN®ZV60 solutions. For all the plots, small panels are introduced to show better the points at low values.

their spectrum is very close to that of the isolated molecule. Also in this case the weight assigned to the monomer should be attributed also to the contribution from weakly (see Table 1) interacting dimers, not involved in hydrogen bonds.

In conclusion, the contribution used to build the fitting functions are those of the isolated molecule, the dimers 1, 2, 3 (Fig. 3b–d) and the trimer 2 (Fig. 3g). In this way we can limit the parameters of the fitting to the strictly necessary ones, thus avoiding redundant parameters which could complicate the fitting procedure, possibly preventing a correct convergence.

In Figs. 6 and 7, we display our results: the fit is very good in all the cases and correctly predict the trends observed experimentally, even in the minor details. This is an excellent result, especially considering that the frequency range of X–H (X = C, N, O) stretching is difficult to be described computationally, since it is affected also by subtle effects which cannot be accounted for in the calculations (anharmonicity in particular). In Fig. 8, the same fitting procedure has been applied to solutions where the solvent is H-GALDEN®ZV60: we find again a very good agreement between the experimental spectra and the result of the fitting. In this case, however, a predominance of non interacting molecules is observed.

Concerning the frequency scaling factors determined by the fitting, average values of 0.9574, 0.9577 and 0.9549 are found respectively for FOMBLIN®M03, GALDEN®D02 and H-GALDEN®ZV60 solutions. The parameters obtained are consistent with the fact that H-GALDEN®ZV60 has the larger dielectric constant (3.6 to be compared with 2.1 for FOMBLIN®M03 and GALDEN®D02), which is expected to determine a general downshift of the IR frequencies of the dissolved species. This effect is indeed confirmed by simulations (see Fig. S3 of the Supplementary Material) where the Polarizable Continuum Method (PCM) [25] is used to include solvent effects.[3]

As already discussed in the previous sections, while increasing the concentration of the polymer one expects an increase of H-bonded species, consistently with the growth of the low frequency broad band assigned to vibrations mainly involving H bonded NH and with the decrease of the bands associated to isolated, non interacting molecules. On these grounds, in order to extract some quantitative informations from the fittings we can consider the plots presented in Fig. 9. They report, for each solvent, the relative amounts of the three species considered as a function of concentrations. The evolution of the amount of the different complexes can be clearly followed to give also a quantitative description of the evolution of the system at the molecular level.

For the first two solvents, it is clearly demonstrated that an increase in concentration causes indeed an increase of hydrogen bonded complex and a decrease of non interacting molecules, consistently with what is usually expected for systems which are able to form dimers.

On the other hand, the peculiar behaviour of H-GALDEN®ZV60 still needs an explanation since in these solutions the hydrogen bonding of the polymer seems to be limited. By looking at the

Table 4
Computed values (B3LYP/6-311++G**) of frequencies (cm^{-1}) and IR intensities (km/mol) for the models shown in Fig. 3 in the C=O stretchings frequency range. Frequency values have been scaled by 0.9688.

	C=O stretch. frequency (cm^{-1})	IR intensity (km/mol)
Isolated	1753	379
Dimer 1	1748	61
	1734	928
Dimer 2	1730	782
	1705	0
Dimer 3	1747	270
	1727	655
Dimer 4	1752	1
	1751	851
Trimer 1	1735	833
	1735	814
	1698	0
Trimer 2	1745	360
	1735	80
	1717	1123

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[3] The results of the calculations obtained by using PCM should be taken only qualitatively to show the direction of variation of vibrational frequencies when using different solvents. Quantitative results should be considered with care since the reliability of the PCM method in reproducing numerically the values of frequencies in perfluorinated systems should be checked more in deep. Indeed, these systems show subtle effects generated by the delicate interplay between intramolecular and intermolecular interactions which require particular attention in modeling.

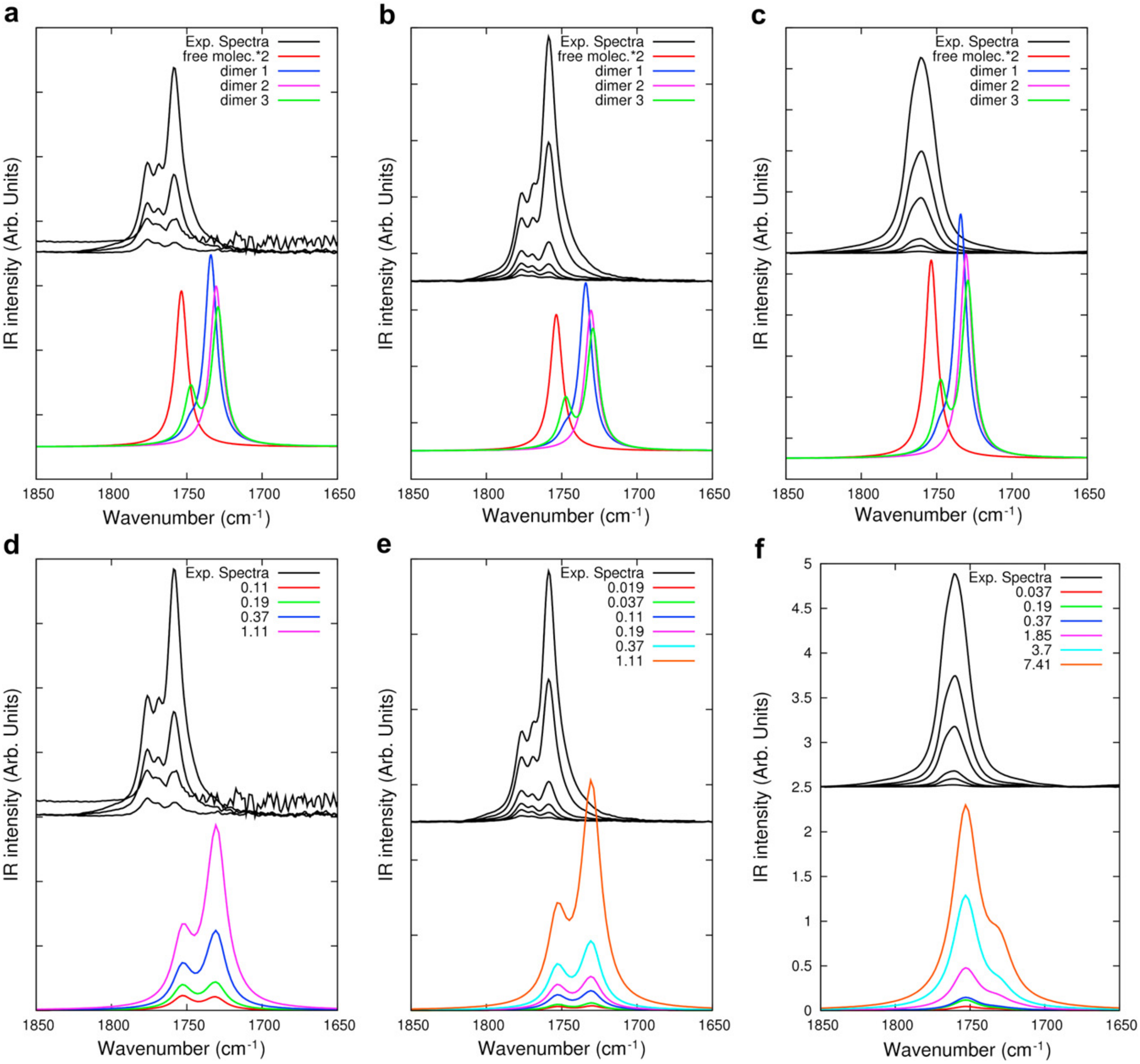

Fig. 10. Comparison among the experimental (spectral subtraction with pure matrix) and DFT computed spectra (B3LYP/6-311++G**, frequency scaling factor = 0.9688) in the frequency range of C=O stretching modes: a) FOMBLIN®M03 solutions b) GALDEN®D02 solutions c) H-GALDEN®ZV60 solutions. Experimental spectra are reported in black and they refer to the same solutions quoted in Fig. 2 for different values of concentration. In the d),e) and f) panels, the sum spectra of FOMBLIN®M03 (d), GALDEN®D02 (e) and H-GALDEN®ZV60 (f) are reported for different concentrations. These sum spectra have been generated by summing the spectra of the isolated molecule, dimers 1,2 and 3 and trimer 2 (B3LYP/6-311++G**, frequency scaling factor = 0.9688), weighted for the coefficients determined by the fitting of the experimental spectra in the NH stretching frequency region (reported in Fig. 9).

structure of the solvent molecule, it could be supposed that hydrogen bonding could be formed between the polymer and the solvent and in particular between the CH group of H-GALDEN®ZV60 and the oxygen of the C=O group of the amide. H atoms in H-GALDEN®ZV60 are indeed acidic due to the presence of fluorine atoms and it has been already demonstrated that hydrogen atoms in similar environment can form H-bonds [26]. Furthermore, this kind of H bond should be very peculiar, since it is expected to induce a blue shift of the stretching frequency of the CH involved in the bridge: it has been indeed defined as new type of H bridge called "blue shifting" or "improper" hydrogen bond [27].

In order to verify whether this peculiar interaction could occur in H-GALDEN®ZV60 solution we carried out calculations where our model molecule is interacting with another model molecule representing the solvent, with the chemical structure: $CF_3CF_2{-}O{-}CF_2{-}O{-}CF_2H$. The computed interaction energy of the complex results to be −3.34 kcal/mol and is thus comparable to those obtained for the models of dimers illustrated in Fig. 3 (see Table 1). This implies that H-bonding between the polyamides and the H-GALDEN®ZV60 solvent is competitive with the formation of the polyamides–polyamides complexes. However, while a blue shift ($\Delta\nu = 28\ \mathrm{cm}^{-1}$) is indeed found in the computed spectra, consistently with previous results on similar systems [27], the experimental spectra do not show a blue shifted component in the CH stretchings frequency range, even for large concentrations of the polyamides in solution.

Alternatively, the lack of H dimers of amides in H-GALDEN®ZV60 solution can be due to its high dielectric constant:

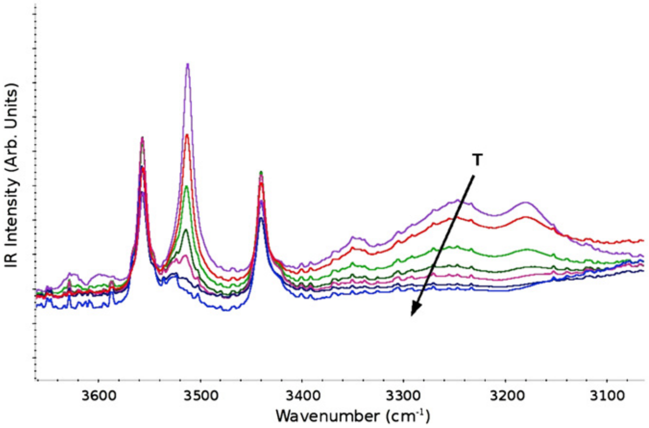

Fig. 11. Experimental IR spectra for Amide in a FOMBLIN®M03 solution of concentration 3% weight/weight for increasing values of temperature from 25 °C to 175 °C (Temperature steps every 25 °C). Spectral subtractions with pure matrix are reported; optical pathlength: (1 mm). The arrow marks the direction of increasing temperature. The whole frequency range (3600–3100 cm^{-1}) of both "free" and "H bonded" NH stretching is shown.

dielectric screening and polarization effects between the polymer and the solvent are larger in H-GALDEN®ZV60 thus possibly preventing amide–amide aggregation.

3.5. Analysis of C=O stretchings

In parallel to the investigation of hydrogen bonding effects on the vibrational observables associated to NH stretchings it is possible to analyze also the behaviour of C=O stretching bands of Amide polymers at different concentrations and in different solvents. It is well-known that hydrogen bonding involving the carbonyl group is responsible for a non-negligible frequency shifts of C=O stretching [12]. On this basis, the frequency of this band was used in a recent paper [15] as a marker for a quantitative analysis of hydrogen bonding effects in other classes of perfluorinated polymers.

In Table 4 we report the values of frequencies and intensities of C=O stretching modes computed for the model systems shown in Fig. 3. Furthermore, we report in Fig. 10 (a–c panels) the comparison among DFT computed IR spectra and the experimental spectra in the frequency range associated to carbonyl stretching mode (1800–1650 cm^{-1}) for the three different solutions previously analyzed. The computed spectra here reported are those obtained by the calculations without any fitting procedure. In Fig. 10 (d–f panels), we use these spectra to build a sum spectrum where each component is weighted for the fitting coefficients reported in Fig. 9 (determined by the fitting *in the NH stretching frequency region*): the evolution with concentration of the main features is described in a very good agreement with the experimental spectra. Indeed, as observed for the NH stretching bands, the spectra in FOMBLIN®M03 e GALDEN®D02 solutions show a peculiar evolution with concentration which can be interpreted as due to the larger and larger contribution of hydrogen bonded molecules. On the other side, no evident evolution in the C=O bands is observed in H-GALDEN®ZV60 solution thus indicating the presence of only a small amount of H bonded species.

This is again in agreement with the interpretation proposed above on the basis of the NH stretchings behaviour.

3.6. Temperature-dependent IR spectra

The analysis reported in the previous sections focused on the dependence on concentration of experimental IR spectra as a consequence of hydrogen bonding effects. The data collected both in the NH stretching and C=O frequency ranges show a parallel behaviour and are well reproduced by DFT calculations. In order to obtain a further experimental validation of our interpretation temperature-dependent spectra have been collected: in Fig. 11 IR spectra for Amide dissolved in FOMBLIN®M03 solvent are shown for increasing temperature from 25 °C to 175 °C. The concentration of the Amide has been chosen and fixed at 3% weight/weight. The range of frequencies of NH stretchings (3600–3100 cm^{-1}) is displayed to reveal the temperature behaviour of the broad feature associated to NH stretching where the H atom is directly involved in H bonding.

From Fig. 11 it is possible to verify that this broad feature loses intensity as far as temperature increases and this can be easily interpreted as a lower content of H bonded complexes in the solutions. Furthermore, by analyzing the "free" NH stretching region we can see that also the band at 3512 cm^{-1} undergoes a marked loss in its intensity with respect to the other two bands at 3560 and 3540 cm^{-1}. On the basis of the previous experimental and computational analysis, the bands at 3512 cm^{-1} has been assigned to "free" NH stretchings belonging to molecules that are involved both as donor and acceptor in H-bonded complexes. The bands at 3560 and 3540 cm^{-1} have been instead assigned to the symmetric and antysymmetric NH stretchings mode of isolated molecules that are not involved in any kind of H bond.

The lowering of intensity of the band at 3512 cm^{-1} with the (temperature-induced) decrease of the fraction of H bonded species confirms the assignments and the interpretation reported above, thus demonstrating the influence of hydrogen bonding in affecting the vibrational properties also of bonds not directly involved in it (that is free NH bonds belonging to H-bonded complexes).

Moreover the Van't Hoff analysis (not reported here) relative to the intensity behaviour of the 3512 cm^{-1} and 3560 cm^{-1} bands allowed us to evaluate a mean energy difference (ΔE) between the associated and free states to be around 5 kcal/mol, in accordance with the predicted values reported in Table 1.

4. Conclusions

The IR spectra of a perfluorinated polyamide dissolved in solvents with different characteristics has been analyzed experimentally and computationally. The peculiar behaviour observed comparing IR spectra at increasing concentration of Amide has been interpreted on the basis of hydrogen bonding involving different molecular complexes whose peculiar structure largely affects the vibrational spectra. In particular, the appearance and the evolution of different bands has been observed in the frequency range associated to NH stretchings of bonds not directly involved in hydrogen bonds and it has been demonstrated that these unusual features are indeed indirect effects of the presence of hydrogen bonding. Furthermore, on the basis of DFT calculations, these bands have been assigned to molecular complexes with a well-defined structure and the analysis of experimental spectra has been carried out in terms of the "content" of these complexes.

This work sheds some new light on the spectroscopic markers of hydrogen bonding going beyond a band assignment which is simply based on empirical correlations as it is frequently used also for quantitative measures. Indeed, despite its general validity and usefulness, the vibrational assignment is not always straightforward and requires great care, as demonstrated by the present case. However, it is shown how a combined computational and experimental study can provide a powerful method of analysis that ranges from the detailed characterization of subtle intermolecular effects to the applications of IR spectroscopy for quantitative determinations.

As illustrated in the introduction, the dosage must be carefully chosen for the chemical formulation of these compounds in order to obtain a correct and suitable behaviour of the material as required in the applications. This work indicates the possible use of IR spectroscopy to this aim, provided that the correct interpretation of the suitable markers is carried out.

Acknowledgements

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Appendix. Supplementary material

Figures of atomic charges on H atoms derived from DFT computed atomic polar tensors for the isolated molecule and dimers, Figure of DFT computed eigenvectors relative to NH stretchings of the isolated molecule and dimers and Figure of DFT computed IR spectra for the isolated molecule by application of the Polarizable Continuum Method. Lists of the optimized geometrical values for all the models investigated by means of DFT computations. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.04.002.

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